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Fixation of atmospheric nitrogen by nanodiamonds[†]

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Very dilute aqueous colloids of a detonation-produced nanodiamond support the growth of fungi, which contain more nitrogen than that present in the nanodiamond as admixtures. We show that the extra nitrogen comes from the fixation of atmospheric N_2 , rather than from the concentration of nitrogen admixtures in the nanodiamond. N_2 fixation can also be achieved using the colloids of an ordinary, nitrogen-free, synthetic diamond. The process (distinct from the known, extremely low-yield photolytic one) is made thermodynamically possible due to the lower (as proven by calorimetry) atomisation energy of carbon in nanoparticles. It converts nanodiamonds into O-, N- and H-enriched solids of variable composition, which lose mass exothermically upon heating in an argon atmosphere, yielding CO₂, H₂O, NO and NO₂ through internal oxidation.

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Introduction

Industrial fixation of N₂ by the Haber–Bosch process is vital for modern civilisation.¹ No viable alternative to this energy-intensive process (consuming 1–2% of the world energy output) has been found yet, hence there is great interest in novel ways to open the N \equiv N bond.² During our recent studies^{3–5} of interactions of detonation-produced nano-diamond (DND)⁶ with water, we observed the formation, in dilute aqueous colloids of DND, of peculiar fibres⁴ identified as fungal gifs with DND particles agglomerated inside them.⁷ Surprisingly, the growth of these fungi was enabled by small (*ca.* 0.05 wt%) amounts of DND in the absence of any apparent source of nutrients, particularly of nitrogen compounds.

Although DND normally contains 1.5-2.3% of nitrogen (originating from explosives),⁶ only a minor part of it is in the form of surface-terminating amino- or nitro-groups, the rest being embedded as defects in the diamond core, where it is not bio-accessible.⁸⁻¹⁰ Nevertheless, we found the fibres to contain more nitrogen (C/N ratios of 20 to 30) than even its total amount in DND (C/N of *ca.* 40, see Table 1).

In the present work, we explore the origin of the extra nitrogen, which can have only two sources: the extraction and concentration of nitrogen impurities from DND, or the fixation

 Table 1
 Elemental analysis (wt%) of the dry residues from the DND colloids and slurries, and C/N weight ratios

	Sample	Treatment	С	Н	N	O ^a	C/N
	DND powder		87.1	0.5	2.2	10.2^{b}	40.7
1	DND colloid	Air-dried, 1 week	69.6	1.2	4.2	25.0	16.6
2	DND colloid	Air-bubbled, 24 h	52.1	1.3	3.6	43.0	14.5
3	DND colloid	N ₂ -Bubbled, 24 h	51.2	1.3	4.8	42.7	10.7
4	DND colloid	Dried at 60 °C, 4 h	86.0	0.3	2.2	11.6	40.0
5	DND colloid	Air-dried, 3 weeks	42.6	3.0	3.4	51.1	12.7
		Compared with 4 ^c	93.6	6.6	7.4	112.3	
6	DND colloid	N ₂ -Bubbled, UV, 11 h	27.2	1.8	1.3	69.6	20.8
7	DND colloid	N ₂ -Bubbled, dark, 11 h	34.4	1.9	2.0	61.7	17.2
8	DND slurry	N ₂ -Bubbled, UV, 11 h	69.6	1.5	2.0	35.5	35.5
9	DND slurry	N ₂ -Bubbled, dark, 11 h	70.5	1.4	1.9	36.9	36.9
	Tomal powder		98.0	0	0	1.0	—
10	Tomal AS, coll.	N ₂ -Bubbled, 2 weeks	35.0	1.5	2.4	61.1	14.9
11	Tomal AR, coll.	N ₂ -Bubbled, 2 weeks	10.6	2.5	2.7	84.3	4.0
a The balance. b Including \sim 1% of metallic impurities. c Assuming the total as 220%.							

of atmospheric N_2 . The former option was ruled out, both by precise mass balance and by replacing DND with a nitrogenfree synthetic diamond. Therefore, we experimentally investigated the possible causes and mechanism of N_2 fixation by a nanodiamond. In view of the recently reported¹¹ photo-catalytic reduction of N_2 to NH_3 due to the release of electrons from a diamond surface into water, we investigated the effect of UV irradiation on the present process.

Experimental

It is known that DND powders are often highly heterogeneous, their chemical composition and surface termination depending

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strongly on the history of detonation and purification. For the sake of uniformity, in all the experiments, we used DND that was freshly prepared in-house by detonating a TNT/RDX (1:1) blend and purified using perchloric acid, as described elsewhere.⁴ 7 separate detonation experiments were carried out, two analyses were performed for each sample. The average composition (e.s.d.): C, 87.1(1.5), H, 0.49(13), N, 2.19(13)%, while sampling the errors of each individual experiment averaged 0.3, 0.1 and 0.06% for C, H and N, respectively (Table S1, ESI[†]). The balance was mostly oxygen, apart from Fe (up to 1.2%) and Si (up to 0.6%) extracted by shock-waves from the walls of the explosion chamber, which gave a non-combustible residue. Evaporation of the DND colloids (entry 1, see below) was also repeated with a commercial DND from Real Dzerzhinsk Co. (Russia) and SDTB Technology (St. Petersburg, Russia), with similar results.

The DND was stirred and then sonicated in high-purity de-ionized water (1 g per 100 mL), the suspension was kept for 3 days to allow precipitation of the solid phase, and the resulting grey turbid slurry¹² (containing about 5% of DND) was centrifuged at 15 000 rpm to yield a clear colourless colloid. The DND concentration varied from 0.02 to 0.07 wt%; 0.05% colloids were used for quantitative experiments. In every case, a sample of pure water was kept under the same conditions for comparison. Primary diamond particles of 4-5 nm were observed by X-ray diffraction (using the Scherrer equation), in good agreement with TEM.⁴ In water, according to DLS,⁵ these particles formed agglomerates of hundreds of nm, as expected for the colloids of such concentrations.¹³ Commercial synthetic diamond powders of 0-0.5 µm size were obtained from Tomal Co (Tomilino, Moscow Region, Russia): type AS powder was prepared directly by crystallisation from Ni-Mn melts, type AR powder was prepared by grinding larger crystalline grains. The colloids were prepared as described above and they showed similar agglomerate sizes. Air or N₂ gas of 99.99% purity was bubbled through 80 mL colloid samples in quartz tubes (28 mm diameter, 200 mm height) using porous glass plugs, at a rate of 0.5–0.7 L min⁻¹, at 16 to 19 $^{\circ}$ C. Two 18 W UV-20 lamps were used for UV irradiation, while the reference sample was kept in the dark.

X-ray spectral microanalysis was carried out on a modernized Cameca (France) Camebax Microbeam electron microprobe (accelerating voltage 10 kV, current 70 nA, exposure 10 s per line, amplitude discrimination mode) and a JSM-6010LA scanning electron microscope (20 kV). TEM images were obtained using a JEOL 2100F field emission gun transmission electron microscope at a microscope voltage of 80 kV.

Results and discussion

Although the formation of a fibrous sediment from DND colloids in air was repeatedly observed before,^{10,14} it is note-worthy that the products were never characterised by elemental analysis, whereas transparent electron microscopy (TEM) revealed only linear chains of DND particles, therefore it was

assumed that the fibres had formed *via* the spontaneous selfassembly of the latter, which was explained by electrostatic effects on nanocrystal faces.¹⁵ To clarify this, we allowed a 0.05% aqueous colloid of DND to dry up naturally in a Petri dish in air at room temperature over *ca.* 1 week. Identical portions of the same colloid were bubbled through either with air or with N₂ gas for 24 h. Then, all the samples were dried at 60 °C to a constant weight (*ca.* 2 h). Elemental analyses of the dry residues, **1**, **2** and **3**, respectively (Table 1), showed all of them to have a C/N ratio much lower than that in the parent DND, further decreasing in the succession **1** > **2** > **3**, with a simultaneous decrease in the carbon content and an increase in the nitrogen content and the balance. All the three samples were studied in triplicate, with standard deviations of **1**.0–1.6% for C, and 0.1–0.2% for H and N (Table S2, ESI†).

In accordance with our earlier observations,⁷ the products were proved to be highly unstable towards vacuum and electron beam, thus during TEM experiments (Fig. 1), the fibres quickly disintegrated, leaving behind a 'skeleton' of the DND particles which had been probably mistaken for the original fibres in the earlier studies (see above). Note that, previously we could obtain satisfactory ESEM images of such fibres only using the environmental mode.⁷ Consequently, the X-ray spectroscopic analyses of 1 on two different instruments gave compositions very similar to that of the parent DND, although both the refractive index (1.65 \pm 0.1) and the density (1.7 \pm 0.1 g cm⁻³) of 1 clearly indicate that it is not a pure ND (which has n = 2.42 and $\rho = 3.51 \text{ g cm}^{-3}$). Thus, C, 48.0 and O, 9.16 wt% determined using the Camebax Microbeam electron microprobe (the balance referring to experimental setup) give the O/C atomic ratio of only 1/7, while a SEM experiment (see Table S3 and Fig. S1, ESI[†])



Fig. 1 TEM images of the residues from the DND colloids, showing the fibre (a), its decomposition under the beam (b and c) and one of the remaining agglomerates of the DND particles (d).

gave 1/10.3, (*cf.* 1/3.7 from elemental analysis). No other elements were found, except insignificant amounts of Fe (from the parent DND, see above) and traces of S. Fe obviously originates from the chamber walls and is an ubiquitous contaminant in the DND.^{6,10} Si is also often extracted by explosion from the Si-containing steel of the chamber walls; as proven by direct experiments^{16a} and by the analyses of shock-synthesized solids.^{16b} The Si content, which was less than 0.6 wt% in the parent DND (from elemental analysis), was not detected in the products. The products yielded negligible amounts of incombustible residues, even compared to the parent DND. Probably, the colloid preparation routine (see the Experimental), especially centrifuging, would have removed nearly all the heavier impurities. Since no other elements were present in any of the reagents, practically all the balance must be oxygen.

To clarify whether the additional nitrogen is concentrated from the DND itself or comes from outside, two identical portions of the colloid were, respectively, dried at 60 °C for 4 h (sample 4) or let to dry up in air over 3 weeks at an ambient temperature and then maintained at 60 °C for 2 h (sample 5). The dry residue of 4 had practically the same composition as the parent DND, while 5 had both a higher proportion of nitrogen (3.4 vs. 2.2%) and a mass 2.2 times greater than that of 4. Hence, the absolute nitrogen content in 5 was 3.4 times higher than that in 4 (see Table 1), while the oxygen content increased tenfold. The slightly lower amount of carbon in 4 may be due to its loss in the form of gaseous products (see above). In contrast, samples of the DND slurry, when dried similarly to 5, showed weight losses of 0.65 to 1.85% compared to the parent DND.

Also, to monitor the possibility of external contamination, every colloid sample was followed by a sample of high-purity water, which was subjected to the same treatment. No nitrogen compounds were detected in any of the control samples.

Thus, the only source of nitrogen enrichment is the fixation of N₂, the mechanism of which is not easy to envisage. Hydrogenated diamonds (including nanodiamonds) possess an unusual property of 'negative electron affinity': their valence band edge (-5.2 eV) is higher than the potential of the aqueous redox couple, which is the Fermi level in water (-5.66 eV),¹⁷ allowing the emission of electrons from the diamond surface into water. This level is way below the energy of any of the reactions opening the path of N_2 fixation (-0.2 to -1.2 eV),^{2,11} but the conduction band edge of diamonds is exceptionally high, 0.3 eV above the vacuum level.^{17a} Therefore, Hamers et al.^{11,17b} suggested that irradiation with UV light, whose $h\nu$ exceeds the band gap width of 5.5 eV, would make diamonds a source of hydrated electrons, powerful reducing agents with energies more than sufficient to initiate N2 fixation. Indeed, they reported the reduction of N2 to ammonia under such conditions, albeit with yields of only a few µg. However, this mechanism seems unlikely here for two reasons: (i) it requires a hydrogen-terminated diamond surface, as oxygen-termination (which is usual after the oxidative purification of a DND) creates a potential barrier and shifts the valence gap maximum below the Fermi level;¹⁸ (ii) the band gap in the DND (3.5 eV)¹⁹ is not as wide as in a bulk diamond (5.5 eV). Nevertheless, we checked whether the present process is photolytic. Two portions of the DND colloid were bubbled with N_2 , under UV irradiation (sample 6) and in the dark (sample 7). The same was done with two portions of the DND slurry, samples 8 (UV-irradiated) and 9 (in the dark). The CHN analysis of the dried residues (Table 1) shows that the effect of irradiation is minor for the colloid and practically nil for the slurry.

To rule out entirely an internal origin of nitrogen, we repeated the experiments with two types of synthetic diamond produced by a conventional static-pressure technique, viz. Tomal AS (black powder) prepared directly by crystallisation from Ni-Mn melts and Tomal AR (grey powder) obtained by grinding larger crystalline grains. Both the materials contained no detectable amounts of H, N or non-diamond carbon, and are composed of 98% of cubic diamond, 1% of oxygen and 1% of the metals, which were used for crystallisation; both formed colloids (similar in properties to those of DND), which after bubbling with N₂ for 2 weeks, gave products 10 and 11, respectively (Table 1). The latter showed the same trends as the DND-derived products: depletion of carbon, massive accumulation of oxygen and moderate accumulation of H and N. This shows unequivocally that nitrogen originates from N₂ and that the outer shells of the DND particles, consisting of non-diamond carbon^{5,10} and surface-terminating non-carbon atoms and functional groups, are not relevant.

The nature of the products, and the state of nitrogen in them, is so far unclear. The solid residues have a fibrous habit, refractive indices ranging from 1.58 to 1.87 and colors varying from brown to grey to green, depending on the carbon content. The X-ray diffraction patterns are not very informative, although they contain non-diamond reflections (Fig. S2, ESI[†]). The IR spectra (Fig. S3, ESI[†]) of the DND-derived products show a strong band in the range of 1346–1348 cm⁻¹, which lies in the range typical for the stretching frequencies of C–N bonds in amines and amides, or N–O bonds in covalent nitrates and is absent in the spectrum of the starting DND (static-pressure diamond has practically no IR spectrum, due to its non-polarity).

The most striking feature is the high (albeit varying) oxygen content, comparable in the air-treated and N2-treated samples - a proof that oxygen originates from water rather than air. Simultaneously observed increase in the H and O contents can, of course, be attributed to the adsorption and/or chemisorption of water. The DND is, indeed, highly hygroscopic and bounds water strongly,^{3-5,20} but the observed O/H atomic ratios are much higher than 2. Although the surfaces of both DND and ordinary diamond can be terminated by oxygen-containing groups,^{6,21} the present products contain a different type of oxygen, as indicated by their unusual thermal behaviour. The TGA/DSC studies (Fig. 2 and Fig. S4–S7, ESI[†]) of all the products in an inert atmosphere (Ar) up to 1000 °C show a continuous mass loss totalling 20 to 35%, with two recognisable steps at 300-400 °C and around 700 °C. It is accompanied by a strong and broad but almost featureless exotherm peak. The mass-spectroscopy analysis of the evolving gases (Fig. 2) revealed H2O, CO2, NO, NO2, small amounts of N₂ and atomic N but no CN or C₂N₂. After the initial peak of H₂O (probably, adsorbed moisture) in the range of 100-200 °C,



Fig. 2 Thermal decomposition of product **3** upon heating in an argon atmosphere. Top: TGA curve (green, left scale) and DSC curve (blue, right scale), bottom: mass-spectra of evolving gases.

there are coinciding maxima of water, CO_2 , nitrogen oxides and N_2/N during the accelerated mass loss between 300 and 400 °C, followed by a larger peak of CO_2 (but little or no water!) at 700 °C. Further heating from 1000 to 1500 °C results in continuous loss of water and then CO_2 . Note that under such conditions, the DND itself shows a very different behaviour: a smaller mass loss attributed to the departure of surface-terminated groups and to gas desorption, and a small endothermic effect attributed to the graphitisation of the diamond.²² These results suggest an 'internal' oxidation of the sample by reactive oxygen already present in it, as do the following observations. When the oxygen-rich product 3 was compressed between Bridgman anvils to prepare dense samples for XRD studies, raising the pressure to 23–25 kbar twice caused a spontaneous detonation, producing white smoke with the characteristic smell of nitric oxides.

Then what is the possible mechanism of the observed N_2 fixation? Excluding the photolytic option (*vide supra*) and the unlikely presence of an unknown nitrogen-fixing organism, let us consider the direct reaction

$$2C + N_2 = C_2 N_2$$
 (1)

Under standard conditions, it is highly unfavourable thermodynamically $(\Delta H = 308.9 \text{ kJ})^{23}$ and requires temperatures above 1400 °C to proceed.²⁴ However, this refers to a bulk diamond with the atomization energy $E_a = 716.7 \text{ kJ mol}^{-1}$; the reaction would be exothermic for atomic carbon ($\Delta H = -1124.5 \text{ kJ}$) or C₂ molecules ($\Delta H = -506.5 \text{ kJ}$). In nanomaterials, the E_a substantially

decreases together with the particle size25 and the reactivity correspondingly increases, due to a high proportion of reactive surface atoms with lower coordination numbers. A 22% decrease in the $E_a(C)$ would make reaction (1) exothermic. In DSC experiments,^{25c} even the agglomerated DND particles of *ca*. 5 nm showed a heat of combustion 30% higher than a polycrystalline diamond with a mean particle size of 146 µm, the reaction commencing ca. 300 K lower. If all the difference is due to the lower E_a of the DND, reaction (1) becomes thermodynamically possible. The above reasoning is indirectly supported by the fact that the exotherms of 1, 2 and 3 upon heating in an argon atmosphere to 1000 °C (see Fig. S4, ESI[†]) amounted to 18.5, 20.4 and 15.8 kJ, respectively, per gram of the entire sample, while the weight losses in this range were 26.2, 16.6 and 27.2%, respectively. Thus, the exothermic effects recalculated for the lost mass only, greatly exceed the enthalpy of combustion of bulk carbon in any form $(32.8-36.2 \text{ kJ g}^{-1})$.²⁶

Of course, this is not enough: it is well known that the greatest obstacle to N_2 fixation is the high activation barrier of opening the $N \equiv N$ bond. For this to happen under ambient conditions, a very efficient catalyst must be present. It is note-worthy, however, that DND does possess catalytic properties,^{10,27} albeit little explored and utilised so far.

Admittedly, C_2N_2 was not detected, which can be due to its rapid hydrolysis (eqn (2)) or oxidation (eqn (3)), both reactions being exothermic with $\Delta H = -47.2$ and -297.5 kJ mol⁻¹, respectively. The composition of the gaseous products agrees better with eqn (3).

$$C_2N_2 + 4H_2O = 2CO_2 + 2NH_3 + H_2$$
(2)

$$C_2N_2 + 3O_2 = 2CO_2 + 2NO$$
 (3)

It is noteworthy that an increase in nitrogen content is always accompanied by an even greater enhancement of oxygen content. A similar correlation was observed in carbon electrode materials that were nitrogen-doped using NH_4Cl , and explained by the higher electronegativity of the N atoms making the adjacent C atoms electron-deficient and thus more favorable sites for O₂ adsorption and O–O bond breaking.²⁸

So far, it was not possible to establish the chemical structure of products **1–10** definitely, but it is noteworthy that their elemental analyses correspond approximately to the formulae $C_5(CO_2)(NO) \cdot 2H_2O(1)$, $C_{11}(CO_2)_2(NO_2) \cdot 2H_2O(2)$, $C_5(CO_2)_4(NO_2) \cdot 3H_2O(3)$, $C_6(CO_2)(NO_2) \cdot 3H_2O(5)$, $C_6(CO_2)_{10}(NO_2) \cdot 8H_2O(6)$, $C_{12}(CO_2)_5(NO_2) \cdot 6H_2O(7)$, $C_{28}(CO_2)_3(NO_2) \cdot 4H_2O(8)$, $C_{30}(CO_2)_4 \cdot (NO_2) \cdot 4H_2O(9)$ and $C_{10}(CO_2)_9(NO_2) \cdot 5H_2O(10)$. The moieties/ molecules shown in these formulae (H₂O, CO₂, NO₂) are those actually observed in the mass spectra (Fig. S5–S7, ESI†). Note that each formulae illustrate the oxygen balance of the products and explain their potential for internal oxidation, similar to that which occurs in explosives.

Conclusions

Water colloids of the DND interact with air or N_2 to yield solid products with a C/N ratio lower than that in the original DND, implying an absolute increase in the nitrogen content. Light is not necessary for this process. These solids also contain large amounts of oxygen, which must originate from water (rather than air), as the treatment of colloids with air and N_2 yields similar products. Water colloids of a powdered synthetic diamond (initially nitrogen-free) also interact with N_2 and yield similar products with a substantial nitrogen content. These results can be explained only by the fixation of N_2 by diamond particles, the mechanism of which is as yet unclear but probably includes the formation of cyanogen (shown to be thermodynamically viable on the nanoscale) and its subsequent hydrolysis or oxidation. Upon heating under an argon atmosphere or when subjected to a high static pressure, the solid products decompose by way of internal oxidation, yielding CO_2 , nitric oxides and water.

Conflicts of interest

There are no conflicts to declare.

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